Centrifugal Contactor Efficiency Measurements

Fuel Cycle Research & Development

Prepared for
U.S. Department of Energy
Material Recovery and Waste Form Development Campaign

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January 25, 2017
FCRD-MRWFD-2017-000276

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SUMMARY

The contactor efficiency of a 2-cm acrylic centrifugal contactor, fabricated by ANL using 3D printer technology was measured by comparing a contactor test run to 5-min batch contacts. The aqueous phase was ~ 3 ppm depleted uranium in 3 M HNO_3, and the organic phase was 1 M DAAP/dodecane. Sampling during the contactor run showed that equilibrium was achieved within < 3 minutes. The contactor efficiency at equilibrium was 95% to 100 %, depending on flowrate.

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1. Introduction

The overarching goal of the Sigma Team for Advanced Actinide Recycle (STAAR) is to develop more efficient separation methods for actinides in support of the goal of sustainable fuel cycles. One approach is to oxidized Am to Am(VI), which would allow for its co-extraction with U(VI), Np(VI) and Pu(VI). Oxidation to Am(VI) followed by solvent co-extraction with the other hexavalent actinides has received considerable attention under this program, resulting in two centrifugal contactor hot tests to date. [1, 2] The most recent hot test was conducted during FY16 using four 2-cm acrylic centrifugal contactors, fabricated by ANL using 3D printer technology. The contactors were supplied as a 4-pack and upon receipt the system was configured such that Stages 1 and 2 were operated in countercurrent extraction mode with stages 3 and 4 operated as countercurrent stripping stages. These contactors are shown in Fig. 1.

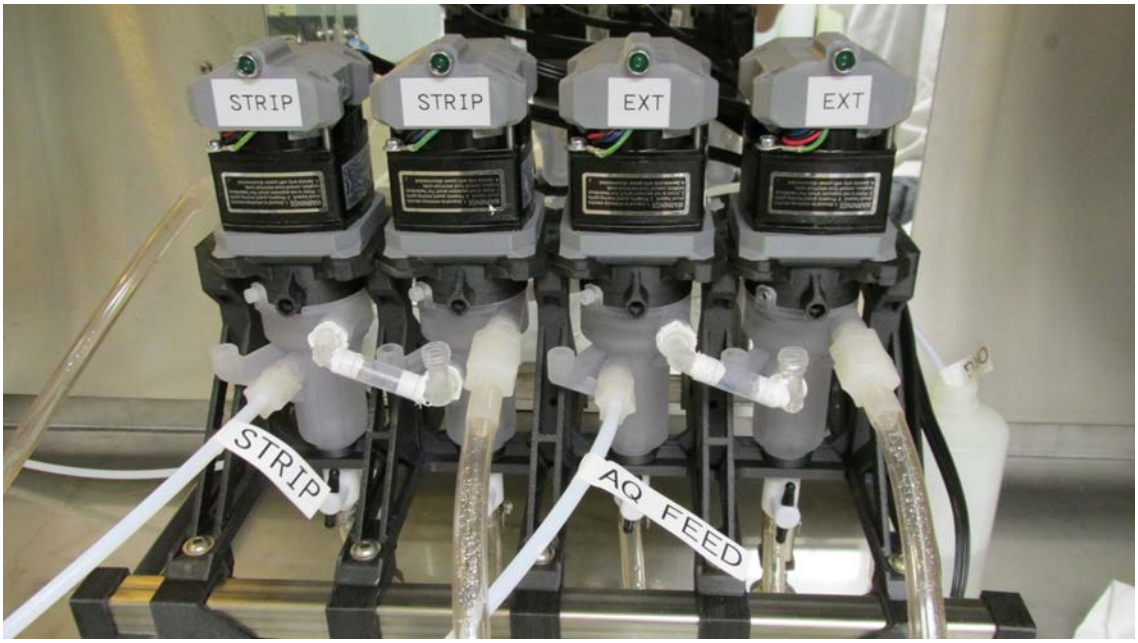

Figure 1. Contactor test bed for the FY16 Am(VI) solvent extraction hot test.

For that test the composite D_{Am} = 1.78 for the duration of test, corresponding to 64 % extracted. This result was lower than for pre-test batch contacts (D_{Am} = 4.2 for a Ru-free, acidity-adjusted raffinate simulant). Lower extraction efficiency was anticipated due to a lower contact efficiency expected for small contactors, and plastic materials of construction. The second stage may have acted as an Am strip due to the increased organic phase contact time, although this conclusion is speculative. To better understand the cause for the low D_{Am} achieved during this contactor test the single stage efficiency of this contactor design was measured here, as was recommended in the FY16 Final Report. [3]

2. Experimental Method

To measure contactor efficiency it was necessary to select a well-characterized extraction system that would eliminate any confounding variables such as effects of Ru, incomplete oxidation, or reduction during the contacts. However, for kinetic reasons it was also desirable to use a solvent system actually under consideration for Am(VI) work. The organic solvent selected was 1 M DAAP/dodecane. The solvent used in the previous hot test was stripped and recycled for use in this efficiency test. Prior to the test the solvent was pre-equilibrated for 1 h with 3 M HNO_3. The aqueous phase for the efficiency test

was 3 M HNO_3, spiked to approximately 3 ppm with depleted U (3.75 uL of 200 g/L ^{238}U stock solution diluted to 250 mL).

A series of batch contacts was completed prior to the contactor test, and designated as the T_0 samples. Then, both phases were sampled at three different times into the contactor run. These multiple samples were obtained to estimate the time necessary for equilibrium to be achieved during a contactor test. The final sample is the contactor equilibrium sample. This entire process was completed at two different contactor flow rates, maintaining a phase ratio of 1.

In addition to the equilibrium contactor distribution ratios, aliquots of the phases of these samples were vortex mixed under batch conditions using 1-min contact times, to generate true equilibrium distribution ratios. The contactor efficiency was then calculated as the ratio of the contactor test D_U, versus the final batch contact D_U.

The D_U is the ratio of the uranium concentration in the respective organic over aqueous phases. Uranium concentrations in both phases were determined using a Thermo X series 2 ICP-MS with a Teflon sample introduction system and platinum cones. During analysis of organic solutions, 0.2 L/min of 20 % oxygen in argon was added to the spray chamber to aid in combustion of the organic material and to reduce build up on the cones. Organic solutions were emulsified with Triton TX100 into the normal 1 % nitric acid solution and stirred for 20 sec used to dilute samples prior to analysis. The same emulsification was applied to the aqueous samples for consistency.

2.1 Contactor Run Test Plan

Contactor operation was performed as follows:

1. Start contactor at 3600 rpm. Use aqueous feed pump to fill contactor with unspiked 3 M HNO_3. Stop feed pump when aqueous flow is observed exiting contactor to the aqueous raffinate bottle. Place feed pump suction tube into spiked feed bottle.
2. Start organic feed pump at 15 mL/min.
3. When organic feed is seen entering the contactor, wait 5 seconds and start aqueous feed at 15 mL/min. This is T_0 for the 30 mL/min test.
4. Pull ~10 mLs effluent aqueous and organic samples at 3, 4 & 5 minutes. Stop pumps and leave contactor running until effluent flows have stopped, then shut contactor off. Record sample times and temperatures.
5. Drain contactor.
6. Disconnect organic and aqueous pump tubing from contactor inlets. Set flow rates to 20 mL/min and measure flow rates to verify.
7. Close drain valve and reconnect pump tubing to contactor.
8. Start contactor at 3600 rpm. Flush aqueous feed pump with unspiked 3 M HNO_3 then use aqueous feed pump to fill contactor with unspiked 3 M HNO_3. Stop feed pump when aqueous flow is observed exiting contactor to the aqueous raffinate bottle. Place feed pump suction tube into spiked feed bottle.
9. Start organic feed pump at 20 mL/min
10. When organic feed is seen entering the contactor, wait 5 seconds and start aqueous feed at 20 mL/min. This is T_0 for the 40 mL/min test.
11. Pull ~10 mLs effluent aqueous and organic samples at 2.5, 3 & 3.75 minutes. Stop pumps and contactor. Record sample times and temperatures.

12. After 3.75 minute sample collection stop all feed pumps. Continue running contactor for ~another minute to allow effluent flows to stop.
13. Shut contactor off.
14. Remove 1 mL aliquots of each collected sample for ICP-MS determination of U concentration. Remove 4 mL of each equilibrium organic and aqueous phase samples into a centrifuge tube and vortex contact for one minute. Then remove three one mL aliquots of each post-contact phase into separate sample bottles for ICP-MS analysis.
15. Drain and rinse contactors and pumps.

3. Results

The contactor test run performed according to expectations. The contactor fill volume was determined to be 25 mL. The total volume of each phase required to run the tests was 212 mL. The distribution ratios that resulted are shown in Table 1:

Table 1. 1 M DAAP/dodecane Uranium Distribution Ratios and Temperatures (ºC)

Preliminary Batch Contacts (T_0)

Sample	D_U	Temperature
1	48.1	21.5
2	51.4	21.5
3	50.5	21.5
average	50.0 ± 1.71	

30 mL/min Experiment

Sampling time	D_U	Temperature
3 min-1	48.6	21.9
3 min-2	48.8	21.9
average	48.7 ± 1.03	
4 min-1	48.8	22.0
5 min-1	52.6	21.9
5 min-2	51.2	21.9
5 min-3	52.7	21.9
average	52.2 ± 0.85	

40 mL/min Experiment		
Sampling time		Temperature
2.5 min-1	47.1	26.1
3 min-1	47.6	26.3
3 min-2	45.7	26.3
average	46.6 ± 1.34	
3.75 min-1	48.1	26.2
3.75 min-2	47.0	26.2
3.75 min-3	46.6	26.2
average	47.2 ± 0.78	
Post-run Batch Equilibrium Contacts		
30 mL/min 5 min-1	50.5	21.4
30 mL/min 5 min-2	50.3	21.4
30 mL/min 5 min-3	51.9	21.4
average	50.9 ± 0.86	
40 mL/min 3.75 min-1	48.6	21.4
40 mL/min 3.75 min-2	50.0	21.4
40 mL/min 3.75 min-3	50.9	21.4
average	49.9 ± 1.17	

It can be seen in Table 1 that equilibrium had already been achieved at the shortest sampling times of 2.5–3 minutes. The data collected in table 1 may be used to calculate the contactor efficiency. This was done by calculating the ratio of the distribution ratios measured during the contactor test, with the equilibrium, post-contactor batch contacts on the same samples. These results are shown in Table 2, resulting in a contactor efficiency of nearly 100 %. As expected, the efficiency is lower at the higher total flowrate due to the reduced contact time of the two phases. However, it can also be seen that the slightly lower distribution ratios found at the higher flow rate were measured at a higher ambient hood temperature. This is consistent with the expected exothermic formation of the DAAP/americium complex. It should be noted that the temporary increase in hood ambient temperature associated with cycling of heaters in the laboratory may not have resulted in actual heating of the solution in the contactors.

Table 2. Contactor Efficiency Calculations (%)

Flow rate	Ratio	Efficiency
30 mL/min	52.2/50.9	103
40 mL/min	47.2/49.9	95

4. Conclusion

The contact efficiency of the 2-cm acrylic centrifugal contactors, fabricated by ANL using 3D printer technology, was measured using uranium extraction form 3 M HNO_3 by 1 M DAAP/dodecane. The efficiency was determined to be 95% to 100 %, by comparison to 1-min batch contacts using the same solutions.